

## STUDIES ON THE SELF-IGNITION OF HIGH-MOLECULAR SUBSTANCES AT LOW TEMPERATURES

### PART II. SELF-IGNITION AND OXIDATIVE DEGRADATION OF COALS AND ANTHRACITE

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The self-ignition temperatures of coals and anthracite, determined by microscopy in an oxygen stream, proved to be close to the points of strong exothermic DTA effects recorded by a derivatograph when the materials were heated in air.

Examination of the ultimate composition and of the i.r. spectra of several coals heated gradually in air up to 330–360° shows that mainly the non-aromatic part is affected by oxygen at lower temperatures.

Utilizing literature data on coal pyrolysis, an attempt has been made to elucidate the mechanism of coal self-ignition at low temperatures. It is considered that the explosion near 200° is due to the dissociation of ether bonds. Break-down of methyl groups bound to aromatic rings is held responsible for the exothermic effect in the range 400–450°. Anthracite self-ignition at 440° is related to the dissociation of aromatic C–H bonds.

Many authors have pointed out that the self-ignition temperature cannot be considered at all as a physical constant. Self-ignition occurs under definite critical conditions. The self-ignition temperature of a solid fuel is a function of various parameters, such as oxygen concentration, particle size, layer-thickness and density of the pulverized fuel, mode and rate of heating, etc. Nevertheless, a number of procedures have been proposed for the determination of the self-ignition temperature of coal.

Using the principle of dynamic DTA for this purpose, many workers determine the temperature where the DTA curve intersects the base-line to pass from the endothermic zone into the exothermic one. The “initial” temperature determined in this way varies with the grade of the coal from 120 to 200°. When thermogravimetry is used, advantage is taken of the property that certain coals increase their weight on being heated in an atmosphere containing oxygen [1]. The temperature of maximum weight is taken to be the self-ignition temperature. For black coal the former varies with the quality, in the range 300–400°.

A procedure has been proposed by Gugel [2] for the determination of the inflammation temperature of coal by means of a Leitz microscope. Dobrevski has applied this to lignites and brown coal and established that they ignite at a temperature near 200° [3].

The aim of this investigation was to make a comparison between the ignition temperature of coals and derivatographic and spectral data of coal oxidation. This comparison is thought to provide information about the mechanism of coal-ignition at low temperature.

## Experimental

### Methods

Simultaneous TG and DTA curves were taken with a Derivatograph in an air stream of 15 l/h.

Infrared spectra were obtained with Unicam 200 PS spectrophotometer, using the potassium bromide disc technique.

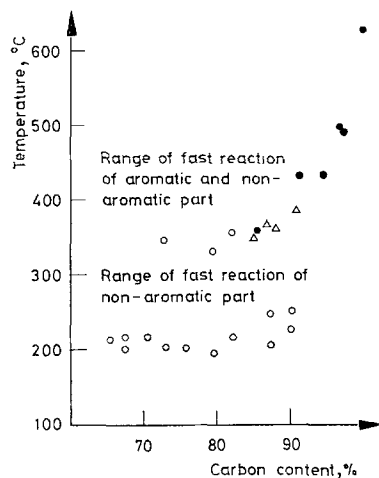


Fig. 1. Temperature of self-ignition carbon content. ○: coal or lignite; ●: combustibles with aromaticity = 1; △: black coals (3)

The temperature of self-ignition was determined according to the principle proposed by Gugel [3], by means of a Leitz microscope. The briquettes (3 mm both in diameter and in height) necessary for this were prepared by compressing the wetted pulverized material. The heating rate was 5°/min, or for some coals 10 or 15°/min. Measurements were made both in oxygen (2 l/h) and air (10 l/h) streams.

### Materials

The investigated combustibles are listed in Table 1. All samples were ground to pass through a 0.200-mm sieve.

## Results

No sign of ignition was observed in the microscope when coal briquettes were heated at a rate of  $5^{\circ}/\text{min}$  in an air stream. Anthracite incandescenced under these conditions. A mild explosion and sparking were observed at  $200^{\circ}$  on heating several types of coals in an oxygen stream. This occurred with other coals only at  $350^{\circ}$ , but they were found to explode at temperatures near  $200^{\circ}$  when the heating rate was increased from 5 to  $10 - 15^{\circ}/\text{min}$ . Thus, it was shown that no matter what their grade, coals and lignites self-ignite in a narrow temperature range near  $200^{\circ}$ .

It is of importance that some of the coals exploded at two different temperature levels: near  $200^{\circ}$  and near  $350^{\circ}$ . The carbon content vs. ignition temperature diagram (Fig. 1) shows two curves; the first indicates coal ignition near  $200^{\circ}$ , the second the ignition of coal at  $350^{\circ}$  and above  $400^{\circ}$  the ignition of other carbonaceous substances: fusain, anthracite, coke and graphite. The aromaticity of these substances being equal to 1 [4], the second curve suggests that coal ignition at the higher temperature level is due to some reaction affecting the aromatic systems. The ignition of fusain, anthracite and coke being impossible at  $200^{\circ}$ , the ignition of coal at this temperature must be related to some reaction affecting its non-aromatic systems.

### *Non-stationary range of interaction between coal and oxygen*

This range was observed when a sufficient amount of coal (1 g), spread on a sample holder composed of 6 piled platinum plates, was heated at a rate of  $5^{\circ}/\text{min}$  in an air stream. The temperature of the sample holder rose rapidly above

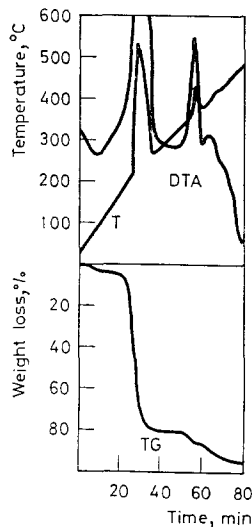


Fig. 2. Xylite from Maritza-East seam. TG and DTA curves recorded in non-stationary range of interaction with oxygen

200° to reach 500–600°, while the temperature in the oven went up to 300° only (Fig. 2).

The quasi-stationary range of interaction was observed by heating a smaller amount of coal (0.2 g), spread on 10 piled platinum plates, the other conditions remaining the same. In this case, the temperature of the sample holder rose almost linearly (Fig. 3). The thermal curves were analogous to those reported

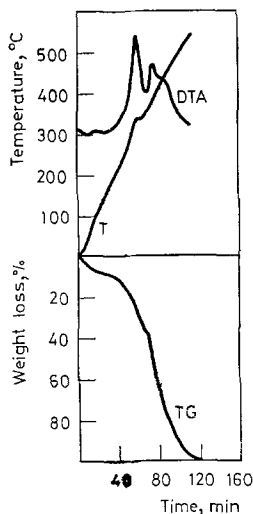


Fig. 3. Xylite from Maritza-East seam. TG and DTA curves recorded in quasi-stationary range of interaction with oxygen

earlier by Weltner [5]. In this range two exothermic zones were established (200–390° and 340–550°), when coal or lignite was heated, and only one exothermic zone at the higher temperatures, when fusain, anthracite, coke or graphite was tested. The temperatures corresponding to the exothermic maxima and the minima observed in the testing of coals are given in Table 1.

#### *Changes in the composition and in the infrared spectra*

Several coal samples were oxidized in a quasi-stationary range of interaction, by heating them up to 340–360°. The solid oxidation products were subjected to infrared spectroscopy to check the structural constituents, the oxidation of which gave rise to the first exothermic peak. The infrared spectra of coals and their oxidation products are shown in Fig. 4. The hydrogen-to-carbon-atom ratio of the solid products is about 1 : 2. Calculations show that as a result of oxidation, xylite (huminite) loses 73%, and the coals 40–50% of their initial hydrogen contents, while the carbon loss is 15–27% (Table 2).

Table 1  
Carbon and hydrogen contents of the samples, temperatures corresponding to the exothermic maxima ( $t_1$  and  $t_2$ ) and to the minimum ( $t_3$ ), and temperatures of explosion in oxygen ( $t_{\text{expl}}$ )

Material	Seam	Mois- ture, %	Ash, % mf	VM				°C			
				C	H	$t_1$ (max)	$t_2$ (min)	$t_3$ (max)	$t_{\text{expl}}$		
				% daf							
Light xylite	Maritza-East	8.4	4.3	67.3	65.8	6.5	290	360	420 (470-sh)	215	
Dark xylite	Maritza-East	10.0	4.6	62.0	67.5	5.4	300	330	420 (470-sh)	220	
Lignite	Maritza-East	10.5	9.5	60.9	67.4	6.1	290	330	440 (450-sh)	205	
Brown coal	Burgas	4.9	6.0	56.0	70.5	6.0	310	340	440	215	
Brown coal	Pirin	7.3	3.8	46.6	73.1	5.3	310	350	470	205**, 345*	
Brown coal	Permik	9.3	10.6	45.5	75.7	5.5	290	340	400	205	
Long-flame coal	Don	7.5	2.5	40.5	79.7	5.2	300	360	460	195**, 330*	
Gas coal	Don	2.6	3.6	34.8	82.2	5.8	320	360	470	215**, 360*	
Coking coal	Balkan	0.4	10.1	25.9	87.8	5.5	(360-sh)	400	500	210**, 245*	
Lean coal	Balkan	0.4	8.4	16.8	90.9	4.7	335	405	500	230**, 260*	
Fusinite	Maritza-East	3.8	6.2	16.9	85.6	2.7	—	—	440	360	
Fusain	Dobrudja	2.1	34.3	9.2	91.5	2.6	—	—	550	435	
Anthracite	Svogue	1.9	12.2	5.8	94.6	2.4	—	—	550	440	
Natural coke	Dobrudja	0.4	48.2	—	96.9	—	—	—	600	500	
Industrial coke	—	0.6	11.2	—	97.0	0.7	—	—	590	495	
Graphite	—	—	—	—	—	—	—	—	810	635	

\* Rate of heating 10°/min. \*\* Rate of heating 15°/min.

Table 2

Carbon and hydrogen contents of the products of coals heated gradually in air up to 330–360°, and  $\frac{H}{C}$  atom ratio of the overall gaseous products

	End of heating, °C	C	H	Change in weight % daf	$\frac{H}{C}$ atom ratio		Degradated	
		in the solid product % daf			of the solid	of the gas	C	H
							% of the initial amount	
Light xylite	340	65.3	2.3	-26.0	0.42	3.28	26.6	73
Brown coal from Pernik	340	67.3	3.9	-14.5	0.50	1.79	24.0	49
Gas coal	360	74.9	3.8	- 5.7	0.58	2.41	14.4	41
Coking coal	350	70.9	3.1	+ 1.1	0.53	1.15	18.6	43

The infrared spectra show that the absorption between 2840 and 2960  $\text{cm}^{-1}$ , due to the non-aromatic part of coal, decreases on heating in air up to 340–360°. The absorption at 1380  $\text{cm}^{-1}$  and near 1460  $\text{cm}^{-1}$ , also related to the same component, similarly diminishes. A strong absorption at 1700–1730  $\text{cm}^{-1}$  in the

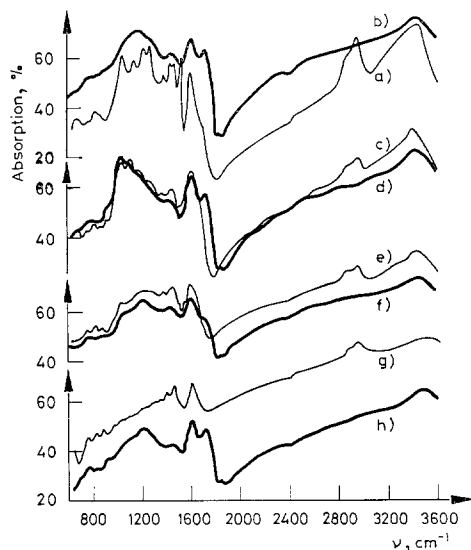


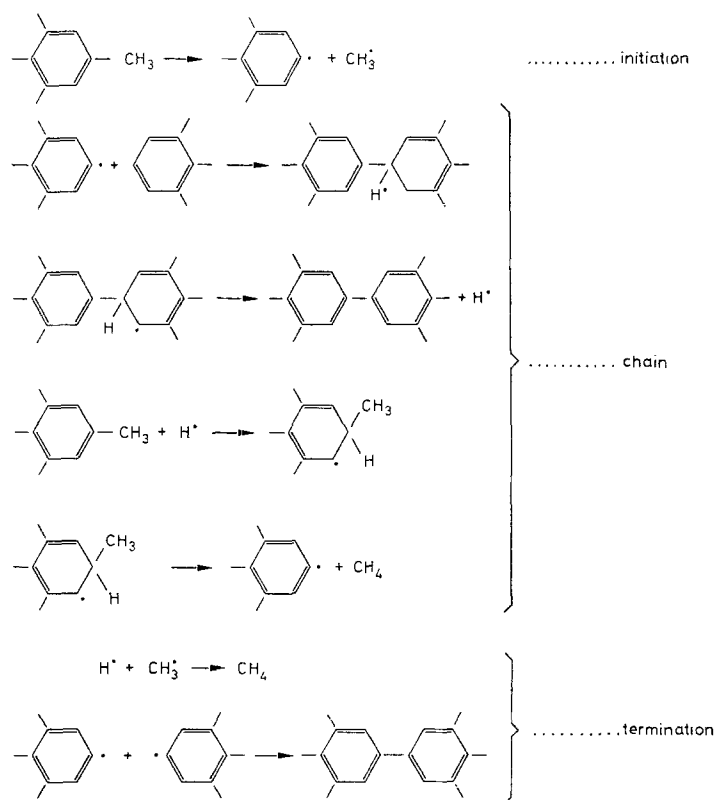
Fig. 4. Infrared spectra: (a) xylite, (b) its residue of gradual heating in air up to 340°, (c) brown coal from Pernik, (d) its residue of heating up to 340°, (e) gas coal from Don, (f) its product of heating up to 360°, (g) coking coal from Balkan, (h) its product of heating up to 350° in air

above spectra may be related to dimerized carboxyl groups, ketones or esters. Their formation indicates the incorporation of oxygen into the organic matter causing an increase in weight of the coaking coal at this stage of the process (Table 2).

Obviously, the non-aromatic part of coal is attacked by oxygen below 340–360°, and its degradation proceeds simultaneously with the oxygen incorporation.

### Discussion

Some evidence about the nature of the two exothermic stages observed on heating coal at a constant rate in air was provided in an earlier work [6]. Taking into consideration the information provided by many authors concerning coal pyrolysis the ignition temperature of coal permits additional conclusions about the mechanism of the interaction between coal and oxygen to be drawn.



*Self-ignition of coal at 200°*

The oxidation of saturated hydrocarbons above 150° is explained by the homolytic dissociation of C–H bonds and by the addition of molecular oxygen or free radicals to double bonds in the olefines. In some cases hydrogen splitting in a neutral atmosphere leads to the formation of hydrogen gas; for coal, however, this could be observed only at 300°. It is well known that coal is oxidized rapidly even at 60–80°. Apparently, the mechanism of the oxidation of coal is not the same as that for hydrocarbons.

Hulanizky and Gloviak [7] investigated the self-ignition of clouds of pulverized brown coal in air and concluded that the induction period is infinitely long at 195°. Since coal is oxidized below 195°, it can be concluded that at this point a change occurs in the mechanism of interaction between coal and oxygen.

When coal is gradually heated in air under conditions of the nonstationary range, oxidative dehydrogenation sets in above 160–170°. The hydrogen-to-carbon-atom ratio of the overall gaseous products formed in the range 170–220–240° varies from 10 : 1 to 6 : 1. The exothermic effect in this range is very low however, although 1/5 of the hydrogen content of the coal is converted into gaseous products. The exothermicity becomes more expressed in the range 210–240°, while the yield of low-molecular hydrocarbons increases nearly 50-fold [8]. These observations support the assumption that a change occurs in the mechanism of interaction between coal and oxygen around 200°.

Včelak, who examined the pyrolysis of brown coal, established that the yield of hydrocarbons, such as ethane, ethylene, propane, propylene and butane increased rapidly in the range 200–300° [9]. This phenomenon may be related to another observation: Angelova and Lazarov found that the unreactive oxygen content decreases when coal is gradually heated up to 250° under nitrogen. Simultaneously, the content of hydroxyl groups in the coal increases. These phenomena were linked with the cleavage of ether bonds [10]. Hence, the change in the mechanism of interaction between coal and oxygen at 200° is very likely a result of the dissociation of weak carbon–oxygen bonds. The self-ignition is most probably due to the oxidation of small fragments.

Coal is known to catalyze the oxidation of certain organic compounds at low temperatures (say 150°), for example the oxidation of ethanol to acetic acid and acetaldehyde [11]. Signs of ignition of the latter have been observed at a temperature as low as 120° [12]. An examination of oxygen-containing low molecular products of coal oxidation at 200° proves necessary in order to elucidate the mechanism of self-ignition at this temperature.

*Oxidative degradation of coal in the range 350–450°*

In their X-ray investigation of the products of coal pyrolysis, Kasatochkin and Razoumova [13] have shown a progressive growth of the lamellae (sets of polycondensed aromatics) above 300–400°. According to Kasatochkin [14], the

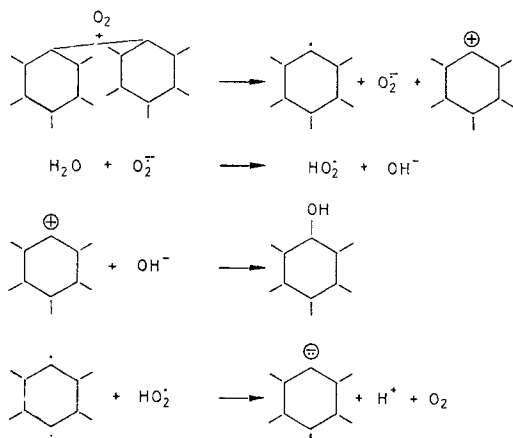


growth is due to the concrescence of adjacent lamellae. The dissociation of aromatic C-H bonds is likely to be the reason for such a process at higher temperatures. The concrescence may be regarded as resulting from a recombination of free aryl radicals, or from addition of free aryl radicals to aromatic clusters. However, below 450°, the rate of dissociation of C-H aromatic bonds is probably very low.

The non-aromatic hydrogen in coal with a 75–90% carbon content is evaluated to be 75–60% of the hydrogen content. The data given in Table 2 show that a proportion of the non-aromatic hydrogen remains unaffected by oxygen when coal is heated up to 360°.

Investigations of the oxidation of polymethacrylic acid have indicated that methyl groups are not attacked up to 380°. These are absent from the residue of the polymer heated in nitrogen at 420°. Under these conditions evolution of methane, propane and butane was established [15]. Hence, it may be concluded that on gradual heating, methyl groups react with oxygen only after the cleavage of CH<sub>3</sub>-C bonds. It can be assumed, therefore, that the non-aromatic hydrogen in the residue of coal heated to 330–360° is mainly bound in methyl groups.

Oelert has found that when coal is gradually heated under nitrogen, the splitting-off of methyl groups bound directly to aromatic rings occurs at 440–450° [16]. This temperature corresponds to the maximum of the second exothermic peak in the DTA curve recorded for the oxidation of coals with carbon contents lower than 83–85%. It follows that the maximum appearing near 450° is due to the splitting-off of methyl groups bound directly to aromatic rings. This reaction, which is assumed to cause the evolution of methane at 440–500° [17], is obviously responsible for lamellae growth. The latter can be regarded as a process analogous to polyphenyl formation in polystyrene pyrolysis [16]. In the case of dissociation of CH<sub>3</sub>-aryl bonds in coal, a chain mechanism may be suggested:



Exothermic reactions resulting at 400° in an atmosphere containing oxygen, the splitting-off of methyl groups bound to aromatic rings probably starts at lower

temperatures than 440°. The evolution of methane from coal with 22% volatile matter starts near 390° [17]. On the other hand, in an examination of coal with 24% volatile matter, Oelert did not find methyl groups other than those attached to aromatic rings. The splitting-off of these groups is thus the probable reason for the evolution of methane and also for the appearance of the second exothermic peak at 400° in the oxidation of coal with a low yield of volatile matter.

In the derivative curves of gradually heated coals Luther et al. [17] found maxima in the range 300–400° (at 330°, 340°, 355°, 370° and 390°), due to the volatilization. The identification of the reactions giving rise to these maxima will contribute to the elucidation of the processes leading to the ignition of coal in the range 330–390°.

In the quasi-stationary range of interaction between coke and molecular oxygen the maximum rate of loss in weight was observed at 600°. The complete conversion of coals into gaseous products at temperatures lower than 550° is probably due to the inhibiting effect of oxygen upon lamellae growth and coke formation.

#### *The self-ignition of anthracite and fusain*

In their X-ray investigation of the char obtained after heating anthracite at several temperature levels, Lermusiaux and Quinot detected structural changes at 500°. At the same temperature they observed a change in the composition of the gaseous product of pyrolysis. At this point, the yield of hydrogen became higher than that of carbon oxide, the latter being the main product of pyrolysis at 400° [18].

By means of derivatograph, Weltner established that anthracite loses weight at 450° when heated gradually under nitrogen. This loss was related to the start of a process analogous to coke formation in bituminous coal. She found that the results of this investigation agreed well with the X-ray results mentioned above, because the pyrolytic process should progress to a certain degree for the coke structure to become observable radiographically [19].

On the other hand, according to Magaril [20], the rates of cracking of naphthalene and other polynuclear aromatic hydrocarbons (pyrene, phenanthrene and chrysene) rise sharply above 450°. On cracking, these hydrocarbons form condensation products and a gas consisting mainly of hydrogen.

The ignition temperature of anthracite (440°), the temperature at which the coke structure begins to develop in anthracite, and the temperature corresponding to a sharp increase in the rate of cracking of polynuclear aromatic hydrocarbons are almost the same; thus, it is clear that the self-ignition of anthracite is due to the dissociation of aromatic C–H bonds.

Fusain with a 93% carbon content ignites at a temperature very near to that of the self-ignition of anthracite. This indicates the absence of paraffinic chains and alicyclic structures. The marked self-heating (Fig. 5) and self-ignition at 360° of

fusinite with an 85% carbon content may be related to the presence of structures decomposing at this temperature at which the aromatic C-H bonds are

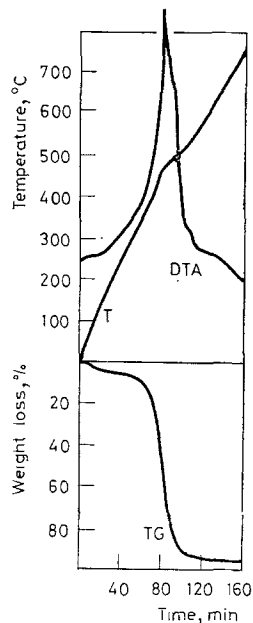


Fig. 5. Fusinite from Maritza-East seam. TG and DTA curves recorded in quasi-stationary range of interaction with oxygen

stable. Fusinite yields an almost continuous infrared absorption spectrum, and the identification of the above structures remains problematical.

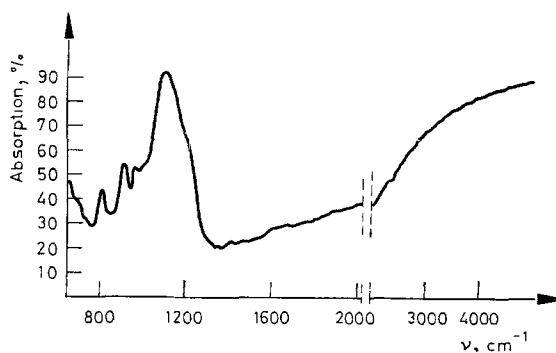


Fig. 6. Infrared spectrum of graphitic oxide

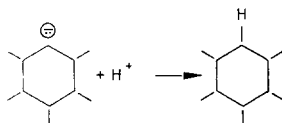
*Some observations on the oxidative degradation of graphite*

The following illustrates the highly complex nature of the mechanism of carbon oxidation. Generator-brush graphite spread in a thin layer on a platinum holder was heated at 850–900° in air for 15–20 min, and was immediately taken out of the furnace to cool down in air at room temperature. This gave a brown-red coloured graphitic oxide containing 0.8% hydrogen. Its infrared spectrum is shown in Fig. 6. The same product was obtained when porcelain holders were used.

It is very difficult to give any definite interpretation of this spectrum. The peak at 810  $\text{cm}^{-1}$ , however, may be attributed to aromatic C–H bonds. Their formation in the oxidative degradation of graphite raises some complicated problems.

Carbon combustion can be explained by the formation of activated complexes or by chain reactions [21]. The mechanism of formation and the nature of the activated complexes in graphite oxidation, however, are not sufficiently elucidated.

The infrared spectrum of graphitic oxide, obtained when graphite was cooled down in air containing water vapour, implies the formation of ion-radicals as intermediates in carbon oxidation. The oxidative hydrogenation of graphite may be regarded as a result of the hydrolysis of ions and ion-radicals:



Charge transfer is likely to be important in the oxidative degradation of coke and aromatic hydrocarbons in solid fuels at low temperatures.

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RÉSUMÉ — On établit que les températures de combustion spontanée de charbons (anthracite) déterminées par microscopie dans un courant d'oxygène sont très voisines de celles des effets exothermiques intenses observés sur les courbes ATD enregistrées sur un "Derivatograph".

L'examen de la composition finale, ainsi que des spectres IR de différents charbons chauffés dans l'air progressivement jusqu'à 330—360°, montre que c'est la partie non aromatique du charbon qui est principalement affectée par l'oxygène aux basses températures.

A partir de données de la littérature relatives à la pyrolyse du charbon, on tente d'élucider le mécanisme de la combustion spontanée du charbon aux basses températures. On considère que l'explosion vers 200° serait due à la dissociation des liaisons éther. On présume, d'ailleurs, que la décomposition des groupes méthyles liés à des noyaux aromatiques est responsable des effets exothermiques dans le domaine de 400 à 450°. La combustion spontanée de l'anthracite, à 440°, est en rapport avec la rupture des liaisons aromatiques C—H.

ZUSAMMENFASSUNG — Es zeigte sich, daß die durch Mikroskopie in Sauerstoffstrom bestimmten Selbstzündungstemperaturen von Kohlen bzw. Anthrazit in der Nähe derjenigen Punkte liegen, welche bei Erhitzung von Kohle bzw. Anthrazit in Luft, vom Derivatographen als Punkte starker exothermer DTA-Effekte registriert werden.

Die Prüfung der Zusammensetzung und der IR-Spektren verschiedener, in Luft allmählich auf 330—360° erhitzter Kohlenreste zeigt, daß bei niedrigen Temperaturen hauptsächlich die nichtaromatischen Teile der Kohle vom Sauerstoff angegriffen werden.

An Hand von Literaturangaben bezüglich der Kohlenpyrolyse versuchte man den Mechanismus der Selbstzündung der Kohle bei niedrigen Temperaturen aufzuklären. Die Explosion in der Nähe von 200° wird dem Aufbrechen von Ätherbindungen zugeschrieben. Die Zersetzung an aromatische Ringe gebundener Methylgruppen wird für den exothermen Effekt im Bereich von 400 bis 450° verantwortlich gehalten. Die Selbstzündung von Anthrazit bei 440° ist mit dem Aufbrechen von aromatischen C—H-Bindungen verbunden.

Резюме — С помощью микроскопа в токе кислорода определены температуры самовозгорания углей и антрацита и показано, что они близки к температурам больших экзотермических эффектов на ДТА-кривых, зафиксированных дериватографом при нагревании углей и антрацита в воздухе. Изучение состава и ИК-спектров различных углей, нагретых постепенно в воздухе до 330—360°, показало, что неароматическая часть угля подвергается главным образом действию кислорода при низких температурах.

На основании литературных данных о пиролизе угля сделана попытка выяснения механизма самовозгорания угля при низких температурах. Высказано мнение, что взрыв около 200° обусловлен диссоциацией простых эфирных связей, а экзотермический эффект в области 400—450° — разрушением метильных групп ароматического кольца. Самовозгорание антрацита при 440° связано с диссоциацией ароматических C—H связей.